Identification of Green Rust in Environmental Compounds Using XANES of Fe-$L_{II,III}$ Edges

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INTRODUCTION

"Green rust" is the name given to a class of iron oxide compounds that play an important role in soil chemistry, but have not been completely characterized either structurally or for their electronic properties. Green rust has been identified as a crucial intermediate phase in anaerobic bacterial corrosion[1]. To understand the role of green rust in the corrosion process, its presence and charge state in various stages of relevant reactions must be identified.

X-ray adsorption near edge spectroscopy (XANES) is well-suited to identifying different charge states of an element. Because of the rich fine structure in the L-edge transition metal spectrum originating in crystal-field splitting multiplet effects, the distribution of charge states in an inhomogeneous sample can be distinguished in a single spectrum. Two different methods are available for measuring the XANES; a total-electron yield method which detects the composition of the "near-surface" region, and a transmission method which averages over the composition of the bulk of a thin section of material. Both methods lend themselves to spectroscopic imaging, using X-ray photoelectron emission microscopy (XPEEM) for near-surface spectro-microscopy, and scanning transmission x-ray microscopy (STXM) for the bulk measurements. We use the BL-7 Spectro-Microscopy Facility STXM and photoemission apparatus in this work.

To produce our green rust, a reaction was initiated between goethite (α-FeOOH) and a solution of $FeCl_2$. By halting the reaction prematurely, precipitates of green rust could be obtained. After drying, the precipitates, dark in color, were mounted on a sample puck. Powders of two reference compounds were also mounted on the puck, $FeCl_2$ (Fe(II+)) and goethite (Fe(III+)) before insertion into an ultra-high vacuum chamber on BL7.0. To prevent contamination of the green rust sample, which is unstable in an oxygen environment, all stages of preparation and introduction into the analysis equipment were performed anaerobically, using an oxygen-free glove box and sealed transport unit. To obtain XANES spectra for each specimen, the sample current to ground was measured as a function of incident photon energy through the Fe $L_{II,III}$ adsorption edge.

RESULTS

XANES spectra for green rust and two reference compounds are displayed in Figure 1. The distinction between Fe(II+) and Fe(III+) charge states is obvious from a comparison of the two reference compounds $FeCl_2$ and goethite (top and bottom, resp.). The green rust sample (2nd from top) has a distinct signature, which resembles most closely the II+ spectrum, but contains a III+ component; the characteristic peak of the III+ signature is seen as a shoulder to the right of the main L_{III} peak. Thus, the green rust can be regarded to first approximation as a superposition of II+ and III+ character. To establish the effect of oxygen contamination, the green rust was later exposed to air for 50 minutes, and reintroduced for a final XANES spectrum (third from top). While there is still mixed II+/III+ character evident in the spectrum, the III+ component now dominates, indicating a conversion of Fe(II+) charge states to Fe(III+).

CONCLUSION

These XANES measurements show that our green rust can be regarded as predominantly in the Fe(II+) charge state, with a component of Fe(III+). Further experiments are necessary to determine whether this represents the intrinsic signature of the green rust, or if it includes some degree of impurity, such as goethite. It is clear that exposure to oxygen results in a conversion of II+ to III+ states. These data will be used as a basis for detecting green rust in smaller concentrations in natural minerals, such as clays, in an effort to better understand the process of biologically induced corrosion of Fe, and the role of 'green rust' compounds in environmental chemistry. Dry- and wet-sample XANES measurements are currently underway for natural clays. The spectra of powders in vacuum will be compared to those of wet samples in solution (from STXM) to determine if the drying process alters the charge state of the Fe.
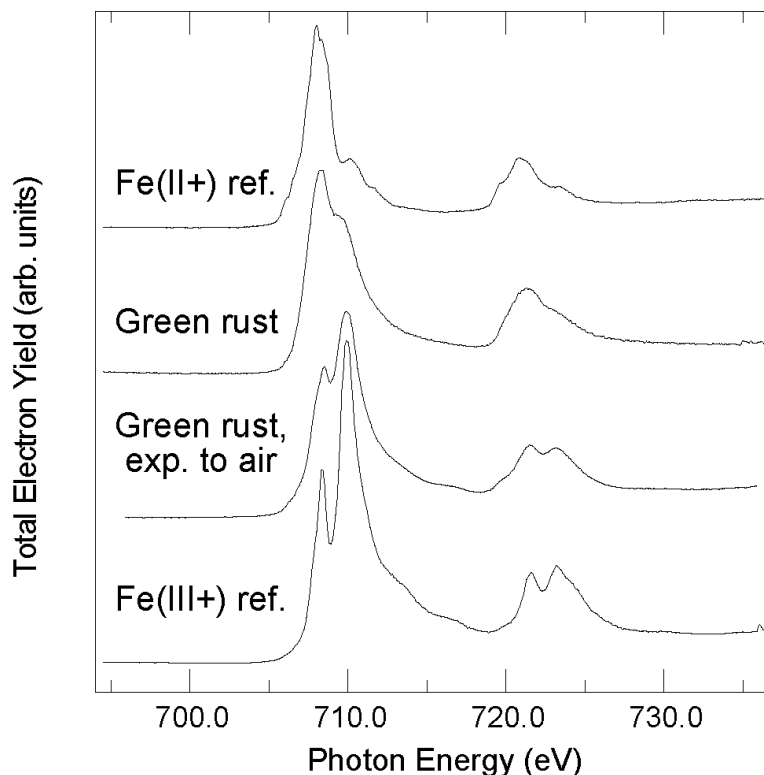

Figure 1. Total electron yield XANES measurements of the Fe-L II,III absorption edges for green rust and reference samples FeCl2 (II+) and goethite (III+). Spectra are normalized to constant background increase through the edges.

REFERENCES

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